

National Physical Laboratory, and the whole of the apparatus was constructed in the workshops of the department.

In conclusion, the author desires to express his thanks to the Committee on Lubrication and Lubricants of the Department of Scientific and Industrial Research, and to Sir Richard Glazebrook and Dr. T. E. Stanton, for the interest taken in the progress of the work.

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*A Study of Catalytic Actions at Solid Surfaces.—III. The Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in Presence of Finely-divided Metals.*

By E. F. ARMSTRONG, D.Sc., F.I.C., and T. P. HILDITCH, D.Sc., F.I.C.

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Until recently, alcohol was always produced by fermenting saccharine materials; acetic acid was obtained as a by-product in making charcoal; acetone was prepared by heating calcium acetate. During the war, both acetic acid and acetone were called for in quantities far larger than would be supplied by such methods; alcohol was also in special demand in connection with the manufacture of cordite; now it is coming into prominence as a possible motor fuel. The effect has been to bring synthetic processes of preparing such compounds to the fore; it is interesting that the methods introduced have nearly all been devised by French chemists.

As far back as 1863, Berthelot was able to show that ethylene obtained from alcohol could be reconverted into alcohol by absorbing the gas in sulphuric acid. The direct synthesis of alcohol from inorganic materials was accomplished when he obtained acetylene by combining carbon with hydrogen at the temperature of the electric arc, as it was possible to hydrogenate acetylene to ethylene.

Berthelot was also the first to attempt the hydration of acetylene, effecting this by the action of sulphuric acid, followed by that of water. Acetaldehyde and crotonic aldehyde were thus produced with other products.

Subsequently it was found that mercuric salts cause a rapid hydration of acetylene to aldehyde in presence of warm dilute sulphuric acid; this discovery has rendered possible the more recent technical processes for manufacturing aldehyde from acetylene.

A simple method of producing acetylene having been provided by the discovery of calcium carbide, the synthetic manufacture of alcohol is now within the range of economic practice, at all events in regions where cheap water power is available.

Alcohol is already being made in Switzerland by the reduction of acetaldehyde by hydrogen in presence of nickel, according to Sabatier's process. The aldehyde is obtained from acetylene by a continuous process of hydration.

Early in the war, a process of manufacturing aldehyde was developed at Messrs. Joseph Crossfield and Sons, Warrington, involving the application of Sabatier's discovery that alcohol is resolved into this compound and hydrogen when passed over heated copper, preferably at about 300 °C. Many hundreds of tons were produced and converted into acetic acid and acetone, the yield under favourable conditions amounting to 90 to 93 per cent. calculated on the alcohol used. From 20 to 25 per cent. of the alcohol is converted at each passage over the metal into an equimolecular mixture of aldehyde and hydrogen. To obtain the former, the vapours are cooled and then passed into an elaborate fractionating column, in which the aldehyde is separated from hydrogen and the excess of alcohol. The technical product contained at least 97 per cent. of aldehyde.

In continuation of our studies of catalytic action at solid surfaces, the dehydrogenation of alcohol and the hydrogenation of aldehyde have both been submitted to careful examination; in the present communication, we desire to draw attention to certain peculiarities in the interactions.

*Hydrogenation of Aldehyde.*—Aldehyde may be converted into alcohol by passing the vapour, together with hydrogen, over either copper or nickel (Sabatier); but in presence of the latter metal, probably owing to the special affinity of nickel for the carbonyl group, the aldehyde is prone to undergo decomposition into carbon monoxide and methane.

The following are the results of experiments in which the ratio of hydrogen to aldehyde was varied from 1·5 to 2·5 molecular proportions of the former to one of the latter.

Table I.

Catalyst.	Temperature.	Vapour hydrogenated.		Time.	Gas-volume change.	Aldehyde recovered.	Alcohol.	
		Aldehyde.	Hydrogen.				Weight.	Yield.
	°C.	gram.	litres.	hours.	litres.	gram.	gram.	per cent.
Nickel ...	120–150	135	120	5	—	49	47	53·6
Copper...	200–210	127	155	3½	34 diminution	40	76	87·6
Copper...	300	114	100	2	5 expansion	34	27	33·7

It is to be noted that aldehydes are more slowly reduced than are the corresponding simple ethylenic compounds. Apart from this, the hydrogenation is comparable with that of an olefinic derivative in presence of nickel or copper and the mechanism of the change is to be considered as identical with that of the latter process.\*

In the experiment with copper at 300°, the amount of alcohol obtained should have involved the withdrawal of about 14 litres of hydrogen; actually, an expansion amounting to about 5 litres was observed, so that about 19 litres of gaseous products of decomposition was obtained. A snap-sample of the gas contained 2 per cent. CO<sub>2</sub>, 2·6 per cent. olefines, 3·7 per cent. CO and 3·7 per cent. calculated to be methane. If the point of equilibrium reached had been the same as in proceeding from the dehydrogenation side, about 85 grm. of alcohol should have been produced; at least, it might have been expected that the amount of aldehyde recovered would have been less than that of the alcohol formed.

*Dehydrogenation of Alcohol.*—The results of typical experiments, using 92 per cent. alcohol, are given in Table II.

The yield of aldehyde isolated compared with that corresponding to the volume of hydrogen measured is given as a percentage in the final column "Ratio CH<sub>3</sub>.CHO : H<sub>2</sub>."

Table II.

Catalyst.	Tem- perature.	Alcohol passed.		Time.	Gas evolved.		Aldehyde obtained.	Ratio CH <sub>3</sub> .CHO : H <sub>2</sub> .
		Grm.	per cent. EtOH.		Litres.	per cent. H <sub>2</sub> .		
Nickel ...	°C. 240-260	945	92	hours, 2	121	60	50	per cent. 35·7
Copper...	300	289	92	1	41	96	72	96
Copper...	295-300	595	92	2	82	98·3	156	97

In the experiment with nickel, the gas evolved contained 60 per cent. H<sub>2</sub>, 20 per cent. CO, 15-17 per cent. methane.

In the case of copper, not only is the ratio of aldehyde to hydrogen close to that calculated but the unchanged alcohol may be recovered almost quantitatively, the yield of aldehyde being about 90-95 per cent. of that to be expected from the amount of alcohol used. There is a striking absence of the secondary products observed when aldehyde together with an excess of hydrogen is passed over the metal at the same temperature.

Nor is the difference to be accounted for by the presence of water in the

\* Cf. 'Roy. Soc. Proc.,' A, vol. 96, pp. 137, 322 (1919).

former case. The alcohol in the experiments recorded in the following Table III had been as fully deprived of water as possible by repeated distillation over fresh lime and finally over sodium; the copper had been heated in a current of dry hydrogen at 300° during several hours. The difference in the gaseous products in presence and absence of water should be specially noted.

Table III.

Alcohol passed.		Tem- perature.	Time.	Gas evolved.						Aldehyde obtained.	Ratio CH <sub>3</sub> CHO : H <sub>2</sub> .
				Litres.	Per cent. analysis.						
					H <sub>2</sub> .	CO <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> .	CO.	"CH <sub>4</sub> ."		
Per cent. EtOH.	Grm.	°C.	hours.								per cent.
Anhydrous	150	300	1	30	76·6	2·4	0·7	3·5	8·7	28	67
92	130	300	1	24	91·0	1·5	0·3	Nil	4·0	38	95
92	2080	330-335	7	582	97·1	—	—	—	—	610	55
92	315	325-330	2	73	98·9	—	—	—	—	95	67
75	855	325-330	3	58	98·0	—	—	—	—	93	83
50	2195	325-330	6	117	91·7	—	—	—	—	176	83

It is evident, (a) that the presence of water improves the yield of acetaldehyde relatively to that of hydrogen. (b) Using alcohol of a given concentration (*e.g.*, 92 per cent.), as the temperature is raised the yield of aldehyde is considerably lessened, although the amount of alcohol decomposed and the volume of hydrogen produced are much increased (at 300° the proportion of alcohol attacked is about 50 per cent. of the total quantity passed as against 20-25 per cent. at 300°). (c) At the higher temperature, the yield may be partially restored by using alcohol containing a larger proportion of water. (d) Even at 300°, if alcohol rendered as anhydrous as possible be used, the yield falls very seriously.

Whatever the conditions, small quantities of by-products are always produced, notably *n*-butyric aldehyde, crotonic aldehyde and ethyl acetate, the total amount being normally of the order of 1 or 2 per cent. of the aldehyde formed.

The results obtained on merely passing aldehyde together with water vapour over heated copper at 300° are recorded in the following Table:—

Table VI.

Vapour passed.		Products obtained after passing over Cu catalyst at 300°.					Total percentage.	
Water.	Aldehyde.	Aldehyde.	Ethyl acetate.	C <sub>3</sub> H <sub>7</sub> . CHO.	Alcohol.	CH <sub>3</sub> . COOH.	Accounted for as aldehyde.	Loss of aldehyde.
125	95	77	} 0·65	0·7	2·2	{ 1·8	80·6	15·1
120	138	102					105	24·0
10	91	46					50	45·0

The proportion of by-products in these experiments is of the order obtained in the actual dehydrogenation of alcohol on the large scale and is not materially affected by the amount of water present. It is clear that water has a considerable protective influence on the aldehyde. To determine whether this protective action extended so far that the reverse action involved in hydrogenation were equally favoured by water, the following experiments were instituted :—

Table V.

Vapour passed.			Gas products obtained after passing over Cu catalyst at 300°.						Loss of aldehyde.
H <sub>2</sub> .	H <sub>2</sub> O.	Aldehyde.	Expn.	Aldehyde.	Ethyl acetate.	C <sub>3</sub> H <sub>7</sub> . CHO.	Alcohol.	CH <sub>3</sub> . COOH.	
lit. 40	grm. 100	grm. 86	lit. 0·45	66	0·4	1·5	3·6	1·9	per cent. 15·1
40	20	79	0·10	31	0·5	2·2	3·3	1·0	51·9

The results show that whilst the aldehyde is protected from decomposition, the effect of even a small proportion of water is to retard hydrogenation considerably—in fact, to render it almost negligible.

Sabatier has attributed the dehydrogenation of alcohol as well as of hydrocarbons by finely divided metals to the supposed aptitude of such metals to form hydrides, the attraction of the metal for hydrogen being regarded as the impelling force.

But it is obvious that the relative affinities of all the agents concerned in such interactions must come into play. In the case of aldehyde, we are inclined to regard the affinity of the carbon compound rather than that of the hydrogen to the metal as of prime importance, indeed, as the determining factor; the marked influence of the metal in causing secondary decomposition is in itself a clear indication that the attraction exercised upon the aldehyde at the metallic surface is considerable.

The protection afforded by water in the dehydrogenating process may be ascribed, from this point of view, to the influence it exercises on the removal of the molecules of aldehyde from the sphere of action. That it has not been found to exercise a corresponding influence on the reverse process is perhaps due to the fact that the conditions cannot well be made the same in the two cases; in other words, the behaviour of a surface at which the aldehyde is being produced towards hydrogen and water may well be different from that of a surface saturated with water towards a mixture of aldehyde and hydrogen.

The general explanation of the changes studied appears to us to be the same as that suggested in our previous communications with reference to simple ethylenic compounds.

The same considerations apply equally to those metallic oxides which have been shown by Sabatier to act similarly to (though less vigorously than) copper on alcohols; the views of earlier workers have involved a mechanism of interaction different in the case of metals from that of metallic oxides; such difference is most unlikely to occur.

Our present hypothesis correlates the action of dehydrogenating metals and metallic oxides with those which are either both dehydrogenators and dehydrators or are exclusively dehydrating in their action; the primary action of the catalyst in all these cases is to effect an association with the carbon compound, the resulting unstable complex then being resolved into other compounds.

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